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Molecular beam epitaxial growth of superconducting $Ba_2DyCu_3O_{6.5}$ thin films at 420 °C using NO_2 as an oxidant

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A superconducting $Ba_2DyCu_3O_{6.5}$ (orthorhombic II phase) thin film is formed on a MgO(100) substrate at 420 °C by molecular beam epitaxial growth using NO_2 as an oxidant. Metal elements Ba, Dy, and Cu are sequentially supplied from *K* cells onto MgO(100) at 420 °C under a flow of 5×10^{-5} Pa of NO_2. The film gradually cooled *in situ* under the identical pressure of NO_2 shows metallic behavior in the normal state and a $T_{c_{zero}}$ of 50 K. The lattice constant of the *c* axis is observed at 11.75 Å, which is known as an orthorhombic II phase of bulk $Ba_2DyCu_3O_{6.5}$. Due to the slow deposition rate, the film thus formed is oriented with the *c* axis perpendicular to the surface in spite of the low-temperature growth condition.

Thin-film growth of cuprate superconducting materials has been studied by a variety of methods. Low-temperature growth of cuprate superconductors has been one of the fundamental problems concerning the mechanism of the crystal growth. Although every cuprate superconducting material known so far has layered structures, not all of them are known to be formed under the layer-by-layer formation mode. $Ba_2YCu_3O_{7-\delta}$ (hereafter the $Ba_2YCu_3O_{7-\delta}$ family is called the "123" compound) system is considered to be formed by the unit-cell epitaxial mechanism.[1] Most of the film growth of "123" compounds is processed at high temperatures such as 600–700 °C.[2–5] Lowering of the growth temperature has been examined, where the typical low-temperature process is shown to be lowered as 550 °C.[4] However, the lower limit of the process is still unknown.

In this letter, we will report on the lowering of the growth temperature by the usage of NO_2 as an oxidant and the *in situ* growth of $Ba_2DyCu_3O_{6.5}$ (orthorhombic II) film. The as-deposited films have a $T_{c_{zero}}$ of $\sim$50 K without any further post-annealing treatment in higher pressure, and are oriented with the *c* axis perpendicular to the substrate surface.

The molecular beam epitaxy (MBE) is carried out with an ultrahigh vacuum system, of which the base pressure of the deposition chamber is 10^{-8} Pa, as has been reported previously.[6–8] Dysprosium, barium, and copper are supplied from separate Knudsen cells using Ta crucibles. Typical cell temperatures are 880 °C for Dy, 1040 °C for Cu, and 600 °C for Ba. The NO_2 flux is used to achieve oxidation of the film during deposition and cooling. NO_2 was supplied through a stainless-steel tube of 1 mm ϕ, which is located 5 mm from the substrate surface, where the amount of the supply is controlled by a variable leak valve.

The substrate MgO(100) (supplied from Earth Jewelry Co. Ltd.: 5×20 mm size of 0.5 mm thickness) is in contact with a Si plate which is resistively heated. The temperature of the MgO is controlled by the current in the Si heater. The temperature of the MgO surface is calibrated by a chromel-alumel thermocouple previously attached to the substrate surface, where the accuracy of the surface temperature is controlled within an error of 20 °C at 420°C. The substrate MgO(100) is rinsed with acetone, followed by a Bi adsorption–desorption cleaning method.[6–8] *In situ* monitoring of the deposition rate is carried out by a quartz thickness monitor, where the total ratio of the elements deposited in the films is determined by electron probe microanalysis [(EPMA) Horiba EMAX-2700] with an energy-dispersion x-ray (EDX) detector. The control of each element is within an error of 10%. The structure of the ultrathin film is observed by the x-ray diffraction [(XRD) Mac Science MXP^3 using a monochromatized Cu$K\alpha$ radiation of 40 kV, 30 mA] pattern. The superconductive property of the films is measured by the standard four-probe method. In order to have a better understanding of the growth mechanism, changes in the surface structure are observed *in situ* by reflection high-energy electron diffraction (RHEED).

On the cleaned MgO(100) surface, as described above, metals are supplied sequentially starting from Ba, followed by Cu, Dy, Cu, Ba, and then Cu. They are supplied under a continuous flow of 5×10^{-5} Pa of NO_2, where the substrate temperature is kept at 420 °C. The nominal growth rate is 0.05–0.07 Å/s. The total thickness of the ultrathin film is about 300 Å. After the deposition, the substrate temperature is held at 420 °C for 15 min, and then slowly cooled down to 300 °C with a cooling rate of 3 °C/min. This cooling process is thought to be effective to achieve the stable orthorhombic II phase, as described later.

The composition of Dy, Ba, and Cu observed by EPMA is 1:2:3, within an error of 10%. A typical XRD pattern of the film thus formed is shown in Fig. 1. Apart from some impurity phases observed at $2\theta=31.1°$, the main feature shows (00*l*) peaks of $Ba_2DyCu_3O_{6.5}$, which confirms that the *c* axis of the film is oriented perpendicu-

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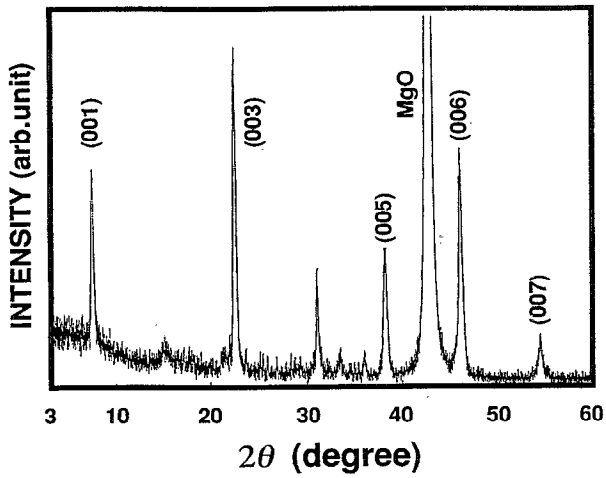

FIG. 1. X-ray diffraction pattern of the $Ba_2DyCu_3O_{6.5}$ thin film formed by MBE with the slow-cooling process, where $c=11.75$ Å.

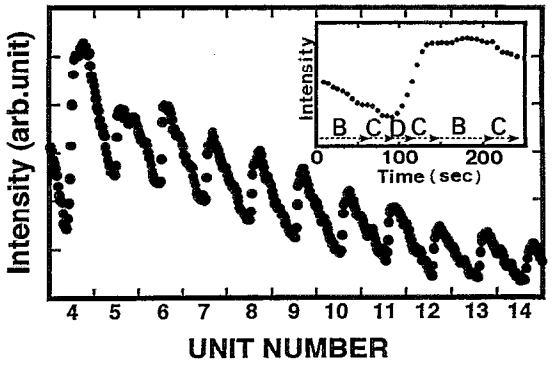

FIG. 3. Intensity of the specular spot observed by RHEED as a function of time during the growth with a sequential supply of the metals and with $P_{NO_2} = 5 \times 10^{-5}$ Pa. The intensity oscillates with the cycle of a unit-cell growth. The relation between the supplying sequence of metals and the intensity change is shown in the insert.

lar to the substrate surface. The lattice constant of the c axis is calculated to be 11.75 Å, which is in good agreement with the orthorhombic II phase ($Ba_2DyCu_3O_{6.5}$).[9] In the film growth of "123" compounds, the a-axis oriented film is known to be formed under a low-temperature growth condition (<600 °C) with the sputter method[5] and the MBE method.[10] However, in our MBE growth at 420 °C, only the c-axis oriented film is obtained. This may be due to the slow deposition rate or to the usage of the NO_2. Further consideration is necessary to clarify the origin that determines the orientation of the film. When the deposition cycle is reduced to half or quarter of a monolayer, the film also shows c-axis orientation, but no RHEED intensity oscillation, as described later, is observed. The temperature dependence of the resistivity of the film is shown in Fig. 2. The figure shows the $T_{c_{onset}} = 70$ K and $T_{c_{zero}} = 50$ K with no transition in the resistivity around 90 K. It is clearly shown here that the $Ba_2DyCu_3O_{6.5}$ orthorhombic II phase is directly formed by the MBE using 5×10^{-5} Pa of NO_2 as an oxidant with an *in situ* slow-cooling treatment.

Changes in the RHEED pattern are observed during the film growth (Fig. 3). When the first Ba layer is deposited onto the MgO(100) surface, where streak pattern due to MgO is clearly seen, this streak pattern gradually disappears and a streak pattern due to the BaO layer appears. The intensity of the BaO streak pattern decreases as the next CuO_2 layer is deposited. After the first unit is completed, the streak pattern due to $Ba_2DyCu_3O_{7-\delta}$ appears at an identical position with the BaO layer, because they have almost the same lattice constant. In the further growth, the intensity of the speculum spot observed in RHEED oscillates, where the cycle of intensity oscillation corresponds to the deposition cycle of a unit cell.

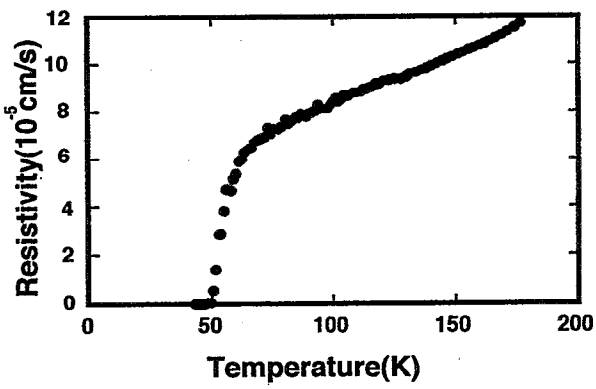

FIG. 2. Temperature dependence of the resistivity of the film shown in Fig. 1 with $c=11.75$ Å.

According to Hammond and Bormann,[11] the optimal epitaxial growth of "123" compounds is obtained near the high-temperature, low oxygen pressure stability limit of $Ba_2YCu_3O_{7-\delta}$. Our low-temperature and low-pressure condition is close to the production of this limit, although the oxidant is different from oxygen. The main frame of the "123" compound is formed in this region. During the slow-cooling process, where the substrate temperature gradually decreases, the condition moves toward the stability line of the orthorhombic phase, resulting in the formation of the orthorhombic II phase.

It is interesting to note that only when the *in situ* slow-cooling treatment is carried out, the c-axis length of the film, 11.75 Å, which corresponds to the bulk $Ba_2DyCu_3O_{6.5}$, is obtained. When the film is taken out without the slow-cooling process, the c axis of such films is usually observed between 11.85 and 12.02 Å. Such a c-axis expansion is reported as a general feature of *in situ* made films, especially when they are grown at a lower pressure.[3] These c-axis expanded films are nonsuperconductive as grown. However, when the films are post-annealed in a 1 atm pressure of O_2 at 350 °C for 16 h, the c axis of these films becomes shorter (for example, in the case of $c=12.02$ Å film, $c=11.88$ Å is obtained), but are still longer than the known value of bulk $Ba_2DyCu_3O_{6.5}$. The c-axis expanded film becomes superconductive after the post-annealing in O_2, which shows $T_{c_{zero}}$ of 60 K and $T_{c_{onset}}$ of 100 K, indicating that this post-annealed film is the mixture of orthorhombic I- and orthorhombic II-like regions, because of a relatively high $T_{c_{onset}}$ and the second transition

region. The *in situ* post-annealing with a higher-pressure O_2 (approximately 1 Pa) at 400 °C also resulted in the formation of the *c*-axis expanded film.

In summary, a superconductive thin film of $Ba_2DyCu_3O_{6.5}$ is obtained at a low substrate temperature of 420 °C and a low NO_2 pressure of 5×10^{-5} Pa. With a slow-cooling treatment the film is superconductive as-grown with the $T_{c_{zero}} = 50$ K. The *in situ* RHEED observation indicates that the growth is realized in a unit-cell growth mode. The frame structure of $Ba_2DyCu_3O_{7-\delta}$ is stabilized when it is oxidized to the orthorhombic II phase, where $\delta=0.5$. For the film with $\delta<0.5$, the length of the *c* axis tends to expand, although it becomes superconductive after the post-annealing treatment in atmospheric pressure of O_2.

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